

PATENT SPECIFICATION

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1,113,409

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COMPLETE SPECIFICATION

Mouldable Plastics Compositions based on ethylene copolymer salts

We, FARBFENFABRIKEN BAYER AKTIEN-
GESELLSCHAFT, a body corporate organised
under the laws of Germany, of Leverkusen,
Germany, do hereby declare the invention,
for which we pray that a patent may be
granted to us, and the method by which it
is to be performed, to be particularly de-
scribed in and by the following statement:

This invention relates to mouldable plas-
10 tics compositions comprising carboxylic
acids containing more than 5 carbon atoms
in admixture with copolymers of ethylene
and α,β -olefinically unsaturated carboxylic
acids containing metal ions.
15 It is known that copolymers of ethylene
and α,β -olefinically unsaturated carboxylic
acids can be reacted with water-soluble
metal compounds. This reaction is accom-
panied by neutralisation of the carboxyl
20 groups present in the copolymers. In the
solid state, plastics compositions of this kind
show the same properties as cross-linked
polymers although they can be fused, in
which state they show the properties of un-
25 crosslinked polymers. Unfortunately, both
the preparation and the processing of salt-
like plastics such as these provide consider-
able difficulties, particularly when high molec-
ular weight copolymers are used as the
30 starting materials and when compounds of
polyvalent metals are employed to neutralise
the carboxyl groups present in the copoly-
mer.

Such polyvalent metals, for example alka-
line earth metals, zinc, aluminium or lead,
35 tend to oversolidify the copolymer when used
in appreciable quantities to neutralise the
carboxyl groups present in it. An excessively
intensive "salt crosslinking" occurs, so that
40 the products cannot be processed or can only
be processed at undesirably high tempera-

tures. In some cases, the materials are also
hard and brittle.

If salts of the alkali metals are used to
neutralise the carboxyl groups present in 45
ethylene copolymers, the difficulties involved
in processing are not on the same scale,
although the alkali metal carboxylate groups
present in the polymers make them undesir-
ably over-sensitive to water.

It is known from Belgian Patent Specifi-
cation No. 611,627 that homopolymers and
55 copolymers of olefinically unsaturated mono-
mers can be mixed with 0.05 to 5% by
weight, based on the total mixture of car-
boxylic acids containing at least four carbon
atoms with a view to improving their prop-
erties, such as their impact strength and
modulus of elasticity.

It is also known from Belgian Patent 60
Specification No. 616,888 that between 0.1
and 5% by weight of carboxylic acids con-
taining 6 to 60 carbon atoms can be added to
homopolymers of monoolefins, of ethylene in
particular, with a view to improving their 65
properties.

Japanese Patent Application No. 16938/1961 (published in Chemisches Zentralblatt,
1965, Vol. 21, No. 2808) relates to a mixture
of polyethylene with 0.003 to 5% by weight 70
of lithium soaps of fatty acids containing at
least 6 carbon atoms, or naphthenic acids.
This is said to inhibit crack growth when the
polymer is heated for prolonged periods.

By contrast, copolymers of ethylene with 75
 α,β -olefinically unsaturated carboxylic acids
and optionally other monomers, in which the
hydrogen atoms of the carboxyl groups
incorporated are completely or partly re-
placed by monovalent or polyvalent metal 80
ions, are used in the process according to
the present invention. The addition of car-

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boxylic acids containing more than 5 carbon atoms, in quantities from 0.1 to 100% by weight based on the copolymer containing metal ions, to an ionically crosslinked and almost unprocessable copolymer of this kind, makes it flexible and eminently processible. It is surprising that homogeneous and clear or transparent plastics compositions showing little or no tendency to disintegrate can be produced. It is assumed that these outstanding properties of the thermoplastic moulding compositions according to the invention are attributable to the interaction between metal ions in the carboxyl-containing copolymer and the carboxyl groups of the carboxylic acids added. The result obtained by the present invention is neither disclosed nor even suggested in the prior art referred to.

One object of the present invention is to improve the processing properties of copolymers of ethylene with α,β -olefinically unsaturated carboxylic acids both during and after neutralisation of the carboxyl groups with compounds of polyvalent metals, and in particular the processing of high molecular weight polymers. Another object of the invention is to produce copolymers of ethylene with α,β -olefinically unsaturated carboxylic acids, which have the lowest possible sensitivity to water. In addition, it is desirable to include in the plastics compositions the inexpensive fatty acids which are available in large amounts.

Accordingly, the present invention relates to a mouldable plastics composition comprising a copolymer of ethylene and an α,β -olefinically unsaturated carboxylic acid and optionally other comonomers, from 10 to 100% of the hydrogen atoms in the carboxyl groups of the copolymer being replaced by monovalent or polyvalent metal ions, whilst the copolymers free of metal ions has a melt index of at least 0.2g/10 mins., which composition contains from 0.1 to 100% by weight based on the copolymer containing metal ions, of a carboxylic acid containing more than 5 carbon atoms.

It is surprising that homogeneous and clear or transparent plastics compositions showing no tendency to disintegrate can be obtained by combining the aforementioned salt-like copolymers with carboxylic acids containing more than 5 carbon atoms because in general, carboxylic acids of this kind are not completely compatible with the aforementioned copolymers. It is also surprising that the addition of carboxylic acids containing more than 5 carbon atoms, in particular aliphatic carboxylic acids containing more than 10 carbon atoms (for example, oleic acid) to hard, ionically cross-linked and almost unprocessable polymeric salts of polyvalent metals (for example the calcium salt of a high molecular weight ethylene-acrylic acid copolymer) makes the

polymeric salts flexible and eminently processible. Neither was it expected that a polymeric salt of this kind, which may be regarded as being completely insoluble both in aqueous and in most organic solvents, would readily absorb the fatty acid added, which becomes integrated as a constituent of the polymer. This is apparent *inter alia* from the fact that the plastics compositions obtained are completely clean, whilst the carboxylic acid incorporated shows no tendency to exude, except when added in large quantities, and even then its tendency to exude is still very limited. Finally, it has also been found that the addition of relatively large quantities of carboxylic acids containing more than 5 carbon atoms is accompanied by little or no deterioration in the ultimate tensile strength of the salt-like polymers, whilst on the other hand their breaking elongation is favourably increased.

Ethylene copolymers containing at least 40 mol % and preferably 50 to 96 mol % of copolymerised ethylene; 1 to 30 mol % and preferably 2 to 20 mol % of copolymerised carboxylic acid and, optionally, polymerised units of other monomers, can advantageously be used as the copolymers of ethylene with α,β -olefinically unsaturated carboxylic acids. The melt index of the copolymers should be at least 0.2 g/10 mins and may even exceed 100 g/10 mins. The melt index is determined in accordance with ASTM-D-1238-57 T.

In addition to the α,β -olefinically unsaturated carboxylic acid(s) and ethylene, the ethylene copolymers of the aforementioned type may also contain further comonomers, in proportions up to 30 mol %.

The following are examples of such co-monomers:

a) Derivatives of α,β -olefinically unsaturated monocarboxylic acids, such as acrylamide, methacrylamide, acrylonitrile, methacrylonitrile and esters of acrylic and methacrylic acid, particularly those with saturated monohydric aliphatic alcohols containing 1 to 20 carbon atoms cycloaliphatic alcohols containing 5 to 7 carbon atoms, phenols, aralkyl alcohols or heterocyclic alcohols, such as esters of the aforementioned acids with methyl, ethyl, propyl, isopropyl, isobutyl, hexyl, octyl or stearyl alcohol, cyclohexanol, methyl-cyclohexanol, benzyl alcohol, phenol, cresol or furfuryl alcohol.

Monoesters of α,β -mono-olefinically unsaturated monocarboxylic acids containing 3 to 4 carbon atoms with dihydric saturated aliphatic alcohols containing 2 to 4 carbon atoms, for example 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, 4-hydroxy-n-butyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate and 4-hydroxy-n-butyl acrylate, can also be employed.

- b) aromatic vinyl and vinylidene compounds, such as styrene, α -methylstyrene, vinyl toluene, p-chlorostyrene or other nuclear-substituted vinyl benzenes;
- 5 c) Esters of vinyl alcohol with carboxylic acids containing 2 to 18 carbon atoms or with hydrohalic acids, vinyl ethers and vinyl ketones, such as vinyl chloride, vinylidene chloride, vinyl acetate, vinyl propionate, vinyl stearate, vinyl ethyl ether, vinyl isobutyl ether, or vinyl amides such as vinyl formaldehyde and vinyl acetamide;
- 10 d) Conjugated dienes containing 4 to 6 carbon atoms such as butadiene, isoprene, 2,3-dimethyl butadiene and chloroprene; and
- 15 e) Propylene, cycloheptatriene or norbornadiene.

Acrylic esters, methacrylic esters and the vinyl esters listed are preferably used as the 20 additional comonomers.

Although ethylene copolymers incorporating these additional monomers may be used, it is preferred to use copolymers of ethylene with α,β -olefinically unsaturated carboxylic 25 acids only.

The olefinically unsaturated carboxylic acids can be incorporated in the polymer in quantities from 1 to 30 mol % and preferably in quantities from 2 to 20 mol %. Preferred carboxylic acids of this kind include acrylic acid and methacrylic acid, although it is also possible to use itaconic acid, maleic acid of fumaric acid or their half esters with alcohols containing 1 to 8 carbon atoms, for 35 example monoethyl acate or fumarate.

It is also possible to use, for the plastics compositions according to the invention, copolymers of ethylene in which the carboxyl group has been introduced by a subsequent 40 operation, for example, oxidation, grafting, hydrolysis or saponification, or by the reaction of an organometallic derivative of the polymer with CO_2 or by the reaction of a reactive group to form the carboxyl groups (for example the reaction of an OH-group 45 with an acid anhydride of a polyvalent carboxylic acid (to form the half ester)).

The copolymers of ethylene with α,β -olefinically unsaturated carboxylic acids and 50 optionally further comonomers, can be prepared by methods known *per se*, for example at pressures from 50 to 300 atm. and at temperatures in the range from 50 to 300°C, by 55 ionic or free radical polymerisation, as described for example in Belgian Patent Specification 679,490, in German Patent Specification Nos. 650,038, 745,425 or in British Patent Specification No. 963,380.

Preparation of the metal salts by neutralising 60 the above-described copolymers of ethylene and α,β -olefinically unsaturated carboxylic acids and optionally other monomers, may be carried out under the conditions of the process disclosed in British 65 Patent Specification No. 1,011,981.

The carboxyl groups of the copolymers are either completely or partly neutralised although at least 10% of the carboxyl groups present are neutralised.

Suitable neutralising agents include the 70 water-soluble or difficultly water-soluble compounds of mono- and/or polyvalent metals of Groups I, II, III, IV-A and VIII of the Periodic System, mentioned in British Patent Specification No. 1,011,981 (cf. Handbook of Chemistry and Physics, Chemical Rubber Publishing Company, 37th Edition, page 392).

Suitable carboxylic acids containing more than 80 5 carbon atoms for addition to the polymeric salts include saturated or unsaturated aliphatic, cycloaliphatic, araliphatic, aromatic and heterocyclic carboxylic acids or carboxylic acid mixtures of natural or synthetic origin with molecular weights in excess of 103, for example naphthenic acids, synthetic fatty acids, cottonseed oil acids, tall oil fatty acids, abietic acid, resin acids, cinnamic acid, phenylbutyric acid, phenylacetic acid, salicylic acid, ω -aminocaproic acid, phynylalanine or N-cyclohexylaminosuccinic acid; it is preferred, however, to use saturated or unsaturated aliphatic monocarboxylic or polycarboxylic acids.

The following are examples of suitable 95 saturated aliphatic fatty acids: caprylic acid, lauric acid, myristic acid, arachic acid, behenic acid, cerotic acid, palmitic acid and stearic acid.

In addition, oleic acid, decylenic acid, 100 palmitoleic acid, dodecylenic acid, linolic acid, linoleic acid, ricinoleic acid, eleostearic acid, parinaric acid, arachidonic acid, ceteoleic acid and nervonic acid, are examples of suitable unsaturated aliphatic fatty acids. 105

Examples of aliphatic polycarboxylic acids are adipic acid, pimelic acid, suberic acid, azelaic acid, undecane dicarboxylic or higher polycarboxylic acids obtained by polymerisation or oxidation processes or, for 110 example, by the copolymerisation of unsaturated carboxylic acids with olefins, vinyl or acrylic compounds or from petrochemicals or by the oligomerisation of natural or synthetic fatty acids, for example so-called dimeric acids.

Carboxylic acids or polycarboxylic acids obtained by polyaddition or polycondensation are also suitable, for example saturated and unsaturated acid polyesters, polyethers, 120 polyamides or polyurethanes containing carboxyl groups.

The carboxylic acids containing more than 5 carbon atoms are added to the salt form of the ethylene copolymers in quantities from 0.1 to 100% by weight, based on polymer containing metal ions, although they are preferably added in quantities from 3 to 50% by weight. Aliphatic carboxylic acids con-

taining more than 10 carbon atoms are preferably used.

Incorporation may be effected by combining the polymer salt and the carboxylic acid in solution, in emulsion or in the solid state at temperatures in the range from 10 to 280°C, for example by directly working the carboxylic acid in dissolved, emulsified or fused form into a dispersion or emulsion of the polymer salt. It is preferred, however, to work the carboxylic acid into the salt-like polymer on mixing rolls or in a kneader at temperatures above 50°C. An alternative method of incorporating the carboxylic acid comprises adding it during preparation of the metal salt of the ethylene copolymer. This alternative eliminates one stage and simplifies handling of the plastics compositions, because the required material is directly formed.

The products obtained by the process according to the invention may be used either in bulk, in solution or in emulsion, for example, for coating purposes. As solids they are suitable as elastomers, extrusion or injection-moulding compositions. Highly transparent coating films and mouldings with a high resistance to chemicals, coupled with favourable mechanical and processing properties, can be prepared from them. The products can be stretched or spun.

Example 1:

The 100% neutralised sodium salt of a copolymer of ethylene and 10% by weight of polymerised methacrylic acid, prepared in accordance with British Patent Specification No. 1,011,981, page 10, (product No. 2 from Table IV), is used: it does not show any tendency to flow in a melt-index apparatus. The material is difficult or totally impossible to process in extruders or injection-moulding machines. These difficulties are caused by the extremely low melt index of the polymer salt. It is intended in the following to demonstrate how the melt index of the material is improved by the addition of stearic acid, thus eliminating any difficulties in its processing. For this purpose, stearic acid is worked in various quantities into separate portions comprising 100 parts by weight of the polymer salt on a grooved roller at 120°C, and the improvement in processibility is followed by reference to the melt index. In every instance, transparent compositions are obtained which can be processed into injection mouldings or films.

	Equivalent of acid % by weight per equivalent of stearic acid Na in the polymer	Melt index g/10 mins.
60	0.0	0.0 no flow
-	5.5 approx. 0.15	0.8
11	" 0.33	2.2
22	" 0.33	5.5
33	" 1.0	6.5
65	50 " 1.5	6.5

Example 2:

The corresponding neutral calcium salt is used in place of the sodium salt of the polymer employed in Example 1. The composition, which does not show any flow in the melt-index apparatus, is difficult to fuse and cannot be processed. Oleic acid is worked in various quantities into this material on a toothed roll whose surface temperature is above 120°C.

Equivalent of oleic
% by weight acid per equivalent Melt index
of oleic acid of Ca in the polymer g/10 mins.

0.0	0.0	no flow	80
5.9	0.16	0.3	80
11	0.3	1.2	80
24	0.65	4.0	80
36.7	1.00	5.0	80

The transparent material can now be processed into films and mouldings. 85

Example 3:

The 100% neutralised zinc salt of a copolymer of ethylene and 3.8% by weight of maleic acid is prepared by rolling the copolymer with zinc acetate at 120°C, followed by removal of the acetic acid liberated in a vacuum dryer at 150°C. This is a material which cannot be processed and which does not flow in the melt index apparatus. 109 parts by weight thereof are kneaded with 26 95 parts by weight of ricinoleic acid for 30 minutes at 140°C in a nitrogen atmosphere, resulting in the formation of a clear, satisfactorily processible polymer composition with a melt index of 15 g/10 mins. 100

Example 4:

Metal salts of the following types of polymer are used in this and the following Examples:

Type 1: Copolymer of ethylene and acrylic acid with a polymerised acrylic acid content of 19.5% by weight and a melt index of 120 g/10 mins.

Type 2: Copolymer of ethylene and methacrylic acid with a polymerised methacrylic acid content of 31% by weight and a melt index of 18 g/10 mins.

Type 3: Copolymer of 9.5% by weight of acrylic acid, 10% by weight of ethyl acrylate and 80.5% by weight of ethylene, with 115 a melt index of 15 g/10 mins.

The 100% neutralised calcium salts of polymers 1 and 2 do not flow in the melt index apparatus. After 15% by weight of oleic acid have been worked in on a kneader at 120°C, the melt indices of these polymers are 9.5 and 1.8 g/10 mins, respectively. The clear polymer-compositions can now be processed. 120

Example 5:

The 65% neutralised aluminium salt of polymer 3 (Example 4) is a highly cross-linked, infusible mass. After 15% by weight of linoleic acid (approx. 0.5% equivalent of acid per equivalent of aluminium 130

55°
5.90

Na salt Neutralised

116 = 116 mole M1

116 - 116 + 0.017 = 85% Neutralised

in the polymer) have been worked into it, the polymer salt loses its crosslinked character, is transparent, satisfactorily processible and has a melt index of 2.8 g/10 mins.

5 Example 6:

The effect of various types of carboxylic acids is demonstrated in the following, with reference to the 100% neutralised calcium salt of polymer 1 (Example 4). A kneader 10 was used for working in which was carried out at 150°C. in the absence of air:—

	% by weight carboxylic acid	Melt index g/10 mins. no flow
15	10 stearic acid	11
	5.0 adipic acid	9
	8.0 azelaic acid	14
	15.0 abietic acid	2.9
	9.0 phenylacetic acid	16
20	11 ϵ -aminocaproic acid	8
	8 copolymer of 37 mol % of acrylic acid and and 63 mol % of ethylene	1.2

25 Example 7:

A polymer of 90% by weight of ethylene and 10% by weight of methacrylic acid, 70% of which is in the form of the sodium salt and which has a breaking elongation of 30 490%, is kneaded with stearic acid at 120°C. After storage for 5 days, the following breaking elongations are measured.

	% by weight of stearic acid	Breaking elongation %
35	—	490
	5	540
	10	551

The increase in breaking elongation improves the blowing properties of the material, 40 and the elastic properties of the films produced from it.

WHAT WE CLAIM IS:—

1. A mouldable plastics composition com-

prising a copolymer of ethylene and an α,β -olefinically unsaturated carboxylic acid and 45 optionally other comonomers, from 10 to 100% of the hydrogen atoms in the carboxyl groups of the copolymer being replaced by monovalent or polyvalent metal ions, whilst the copolymer free of metal ions 50 has a melt index of at least 0.2 g/10 mins, which composition contains from 0.1 to 100% by weight, based on the copolymer containing metal ions, of a carboxylic acid containing more than 5 carbon atoms. 55

2. A mouldable plastics composition as claimed in claim 1, which contains from 3 to 50% by weight, based on the copolymer containing metal ions, of a carboxylic acid containing more than 5 carbon atoms. 60

3. A mouldable plastics composition as claimed in claim 1 or 2, wherein the carboxylic acid containing more than 5 carbon atoms is an aliphatic carboxylic acid containing more than 10 carbon atoms. 65

4. A mouldable plastics composition as claimed in any of claims 1 to 3 wherein the copolymer comprises at least 40 mol % of ethylene, 1 to 30 mol % of an α,β -olefinically unsaturated carboxylic acid and optionally 70 up to 30 mol % of other comonomers, the hydrogen atoms in the carboxyl groups of the copolymer being completely or partly replaced by ions of a metal of Group I, II, III, IV-A or VIII of the Periodic System (as 75 hereinbefore specified).

5. A mouldable plastics composition as claimed in claim 1 substantially as described with reference to any of the Examples.

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